Untangling the Details of North Sea Crude Oil

Sundberg, Jonas Folke; Jensen, Annette Eva; Feilberg, Karen L.

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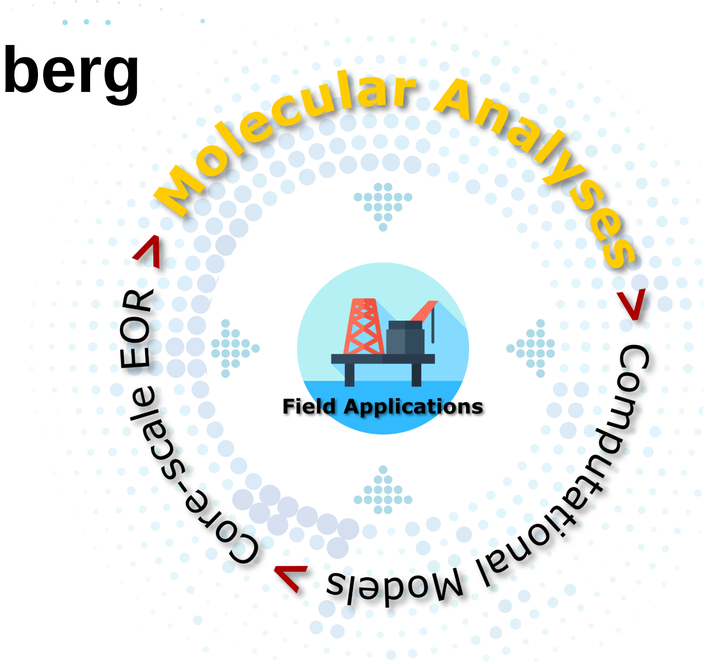
Jonas Sundberg, Annette Eva Jensen, Karen L. Feilberg

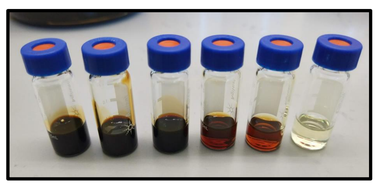
Reservoir Fluid Characterization

A detailed knowledge of the molecular composition of crude oil and reservoir fluids is fundamental to understand its formation, physical properties and macroscopic behavior. Our objective is to study compositional changes that occur during recovery processes, and gain a better understanding of the underlying mechanisms on a molecular level. Additionally, parameters that correlates to maturity, biodegradation and oil genetics are employed to understand migration patterns. The results will provide input for computational models that links laboratory-scale enhanced oil recovery (EOR) experiments to theory, and ultimately field applications.



Sample Set

Geochemical parameters were determined for a sample set consisting of 5 oils and 2 condensates from different fields and wells in the Danish North Sea. The condensates are visually distinguishable based on colour, and are lighter than the crudes which also is evident in the data.

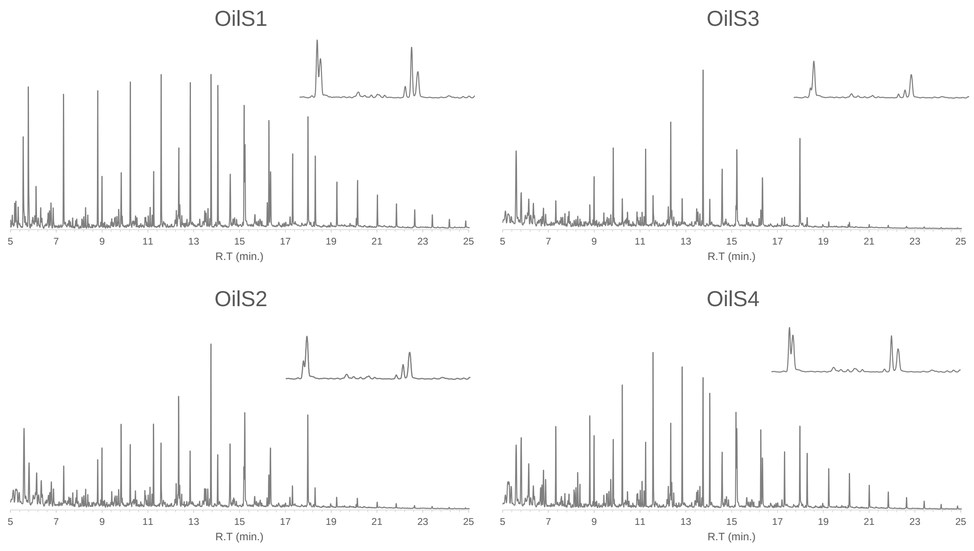


From left to right: OilS2, OilS3, OilS4, OilS5, CondS1-a, CondS1-b

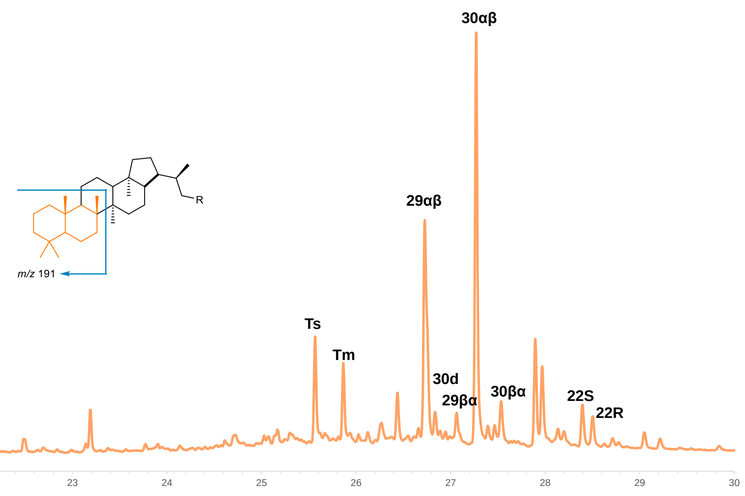
Maturity and Biodegradation

Semi-quantitative parameters used for maturity, biodegradation and oil source correlation are based upon peak area ratios and should be used with care. Issues such as co-elution, and integration parameters affects the data and interpretation and the values must be used in relation with others and as indications, not absolute truths. Compounds were identified by a combination of deconvolution of high-resolution data and comparison of retention using a reference sample (NGS NSO-1) of known composition.

The alkane distribution is noticeable different between OilS1 and the other samples. Maturity parameters indicate that these oils are of similar thermal maturity, and the difference is likely due to slight biodegradation. Ratios of Pr/*n*-C17 and Ph/*n*-C18 add further evidence, as biodegradation affects linear hydrocarbons before branched. OilS2 and OilS3 are the most affected samples. For the condensates, the distribution is shifted towards lighter hydrocarbons as expected. Only very low levels of saturated biomarkers were detected in the condensates, which indicates that evaporative fractionation / gas-condensate migration in the source has taken place.



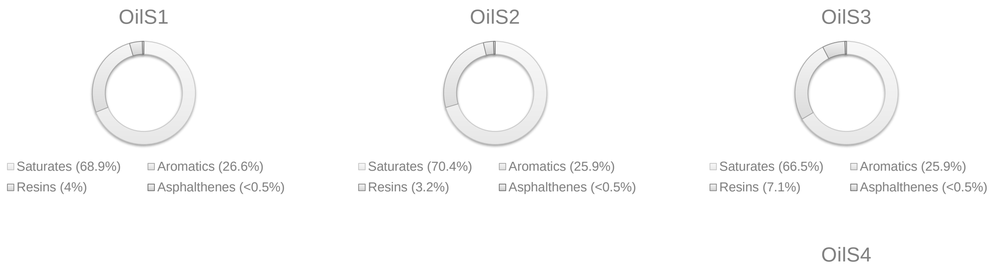
Distribution patterns for saturated hydrocarbons. Insert shows the *n*-C17, pristane, *n*-C18 and phytane region.



Chromatogram of polycyclic terpanes (measured using *m/z* 191) in the sample from OilS2.

Group-type Analysis

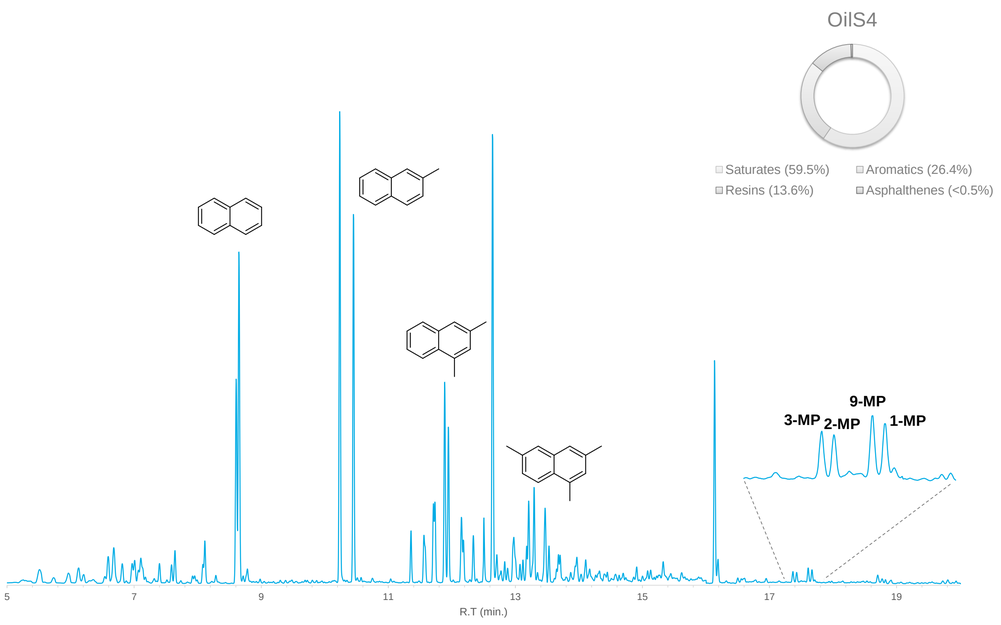
The crude oil samples show typical distributions of saturates and aromatics, with OilS4 having slightly higher content of polar components than the others. The two condensates show a high concentration of light hydrocarbons and monoaromatics, however full SARA-distribution was not determined due to lack of method specificity for these type of samples. The oils have low asphalthene content, and due to the high uncertainty associated with asphalthene precipitation at these levels, values are reported as <0.5% without further specificity. The percentage of resins is back-calculated.



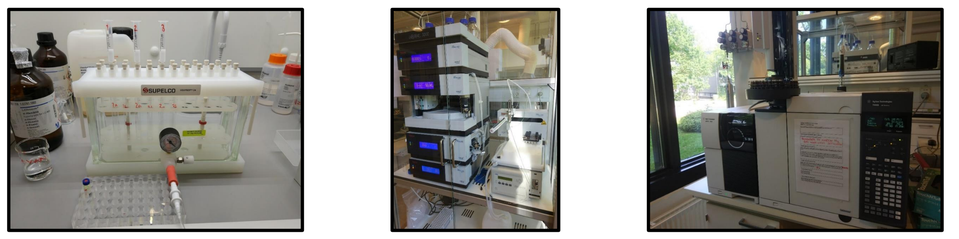
Geochemical Parameters

Sample	Type	*n*-Ca	*n*-Cb	*n*-Cc	Pr/*n*-C17	Ph/*n*-C18	Pr/Ph	Wax	CPI1	OEP1	Ts/(Ts/tm)	30d/(30d+29ba)	22S/(22S+22R)	30αβ/(30αβ+30βα)	MPI1	MPDF1
OilS1	Oil	1.53	1.50	1.16	0.55	0.58	0.94	0.63	1.00	0.98	0.62	0.44	0.57	0.87	0.81	0.42
OilS2	Oil	1.08	1.41	1.45	1.93	1.38	1.15	0.63	1.01	0.93	0.60	0.45	0.57	0.92	0.68	0.41
OilS3	Oil	0.98	1.15	1.32	2.37	1.73	1.05	0.55	1.00	0.95	0.59	0.37	0.56	0.89	0.39	0.28
CondS1-b	Cond.	5.85	1.99	1.55	0.82	0.59	1.58	0.75	1.01	0.97	-	-	-	-	0.50	0.40
CondS1-a	Cond.	2.81	1.10	1.28	0.89	0.83	1.05	0.57	1.01	0.96	-	-	-	-	0.76	0.47
OilS4	Oil.	1.12	1.39	1.86	0.72	0.71	1.03	0.71	1.02	0.98	0.64	0.46	0.57	0.90	0.67	0.41
OilS5	Oil.	1.24	1.06	1.30	1.06	0.98	1.00	0.57	0.99	0.97	0.62	0.40	0.53	0.95	0.81	0.45

***n*-Ca**	∑(*n*-C15 - *n*-C10)/∑(*n*-C20 – *n*-C15)	**OEP1**	(*n*-C25+6*n*-C27+*n*-C29)/(4*n*-C26+4*n*-C28)
***n*-Cb**	∑(*n*-C20 - *n*-C15)/∑(*n*-C25 – *n*-C20)	**Ts/(Ts/Tm)**	Ratio of C27 18α-trisnorhopane II (Ts) and C27 17α-trisnorhopane (Tm).
***n*-Cc**	∑(*n*-C25 - *n*-C20)/∑(*n*-C30 – *n*-C25)	**30d/(30d+29βα)**	Ratio of C30-diahopane and C29-normoretane.
Pr/n-C17	Pristane/n-C17	**22S/(22S+22R)**	Ratio of R/S isomers of C32 - 17α (H),21β(H)-hopanes
Ph/n-C18	Phytane/n-C18	**30αβ/(30αβ+30βα)**	Ratio of C30-hopane (30αβ) and C30-morethane (30βα).
Pr/Ph	Pristane/Phytane	**MPI1**	1.5x(2-methylphenantrhene+3-methylphenantrhene)/(phenantrhene+1-methylphenantrhene+9-methylphenantrhene)
Wax	*n*-C17/(*n*-C17/*n*-C27)	**MPDF1**	(3-methylphenantrhene+2-methylphenantrhene)/(3-methylphenantrhene+2-methylphenantrhene+9-methylphenantrhene+1-methylphenantrhene)
CPI1	0.5x[*n*-C25+*n*-C27+*n*-C29+*n*-31)/(*n*-C24+*n*-C26+*n*-C28+*n*-C30)+(*n*-C25+*n*-C27+*n*-C29+*n*-C31)/(*n*-C26+*n*-C28+*n*-C30+*n*-C32)]		



Polycyclic aromatic hydrocarbons in OilS3 , where alkylated bicyclic aromatics are the major components. Insert shows region with methylphenanthrene isomers used as maturity indicators.



Experimental Details

Solid Phase Extraction

Crude oils and condensates were fractionated into saturated and aromatic hydrocarbons using Phenomenex Strata EPH solid phase extraction columns. The SPE columns were conditioned with CH_2Cl_2 and *n*-hexane, whereupon solutions of crude oil in *n*-hexane were combined with internal standards and loaded onto the column. Saturates were eluted with *n*-hexane followed by elution of aromatics using CH_2Cl_2. Solvent volume was reduced under a gentle stream of N_2, avoiding evaporation to dryness to minimize loss of volatiles. Each sample was processed and analysed in three true replicates.

GC-MS

Mass spectrometry analysis was carried out using an Agilent 7890B gas chromatography oven coupled to either a 7200B GC-HRAM-QTOF of 5977B MSD mass spectrometer. Compounds were separated on a 30 m DB-5MS (0.25 mm I.D., 0.25 um film thickness) fused silica column using a temperature gradient from 50 C (1 min. h.t.) to 320 C (10 C/min., 8 min. h.t.), constant flow He carrier gas at 1.5 mL/min. PAHs were quantified using a 7-point calibration curve prepared from reference standards measured in SIM-mode. Concentrations of alkylated homologs were calculated using response factors of the the parent unsubstituted compound. Linear hydrocarbons were quantified using a 5-point calibration curve prepared from a reference mixture containing C8 - C40. Saturated biomarkers were monitored at m/z 177, 191, 205, 217, 218, 231 and 259. A reference sample containing a mixture of saturated hydrocarbons and polycyclic aromatic hydrocarbons of known concentration was injected every 10th sample to monitor instrument performance.

Saturates, Aromatics, Resins & Asphaltenes

SARA-Analyses was carried out on a Dionex UltiMate 3000 semi-preparative HPC-system. Separation of saturated and aromatic hydrocarbons were carried out using a Thermo Scientific Hypersil Gold NH2 and a Hypersil Silica column connected in series. Saturates and aromatics are separated using an isocratic n-hexane elution profile, where resins are heavily retained on the first column. Resins were then removed from the column by reverse-flow gradient elution using a mixture of chloroform and 2-propanol. A RefractoMax RI521 detector was used for quantification of saturates, and DAD-detection for aromatics. For quantification, a four-point calibration curve were constructed using hexadecane, toluene, naphthalene and phenantrhene standards. Asphaltene content was determined gravimetrically by dissolving 2 mL of crude oil in 5 mL CH_2Cl_2 :MeOH (93:3 v/v) followed by addition of 40-fold excess *n*-heptane. The resulting solutions were stored at 4 °C for 24 hours. Any formed precipitate was collected by filtration, washed with *n*-heptane and dried until stable weight.

Quality Control

Two crude oils of known composition (NGS NSO-1 and NIST CRM 2779) were used as internal quality control during fractionation and analyses.